

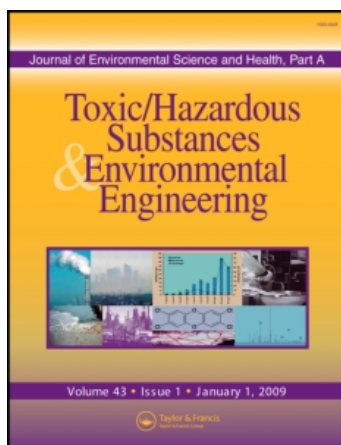
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Pyrolysis of Foundry Sand Resins: A Determination of Organic Products by Mass Spectrometry

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Pyrolysis-gas chromatography-mass spectrometry (MS) was used to identify the major organic products produced by pyrolysis of three foundry sand resins: (i) Novolac and (ii) phenolic urethane (PU) (both phenol-formaldehyde based resins) and (iii) furan (furfuryl alcohol based resin). These resins are used in the metal casting industry as a “sand binder” for making cores (used to produce cavities in molds) and molds for nonferrous castings. During the casting process, the cores and molds are subjected to intense heat from the molten metal. As a result, the organic resins undergo thermal decomposition and produce a number of complex organic compounds. In this study, the organics were tentatively identified by MS after pyrolysis of the resins at 750°C. The major thermal decomposition products from the Novolac, PU, and furan resins were derivatives of phenol, benzene, and furan, respectively. Compounds identified that are of potential environmental concern were benzene, toluene, phenol, *o*- and *p*-xylene, *o*- and *m*-cresol, and polycyclic aromatic hydrocarbons. Pyrolysis of the Novolac resin resulted in the generation of the most compounds of environmental concern. Because there is interest in beneficially using foundry molding sands in manufactured soils and other agricultural products, it is necessary that organic thermal decomposition products be identified to ensure environmental protection.

Key Words: Foundry sand; Furan; Furfuryl alcohol; Novolac; Phenol-formaldehyde; Phenolic urethane; Polymers; Pyrolysis; Resins.

INTRODUCTION

During the metal casting process, molten metal is poured into a mold with an interior of a desired shape. For castings that require a hollow interior, sand cores are used. The sand cores are made using resin-coated sand prepared by a

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number of different processes and with binders containing unique chemistries. Depending on the casting material, the resin binder undergoes thermal decomposition and a variety of organic products is generated, which depends on the binder composition. The thermal decomposition products condense in the molding sand and are emitted into the air during casting, cooling, and casting shakeout.

Resins commonly used by the foundry industry are Novolac, phenolic urethane (PU), and furan. Novolac and PU resins are both phenol-formaldehyde (P-F) based resins, whereas the furan resin is a furfuryl alcohol based resin. Figure 1 shows the general structure of the resins before cross-polymerization. Novolac resin is formed by an acid-catalyzed reaction of excess phenol with formaldehyde. Cross-polymerization of the Novolac oligomers occurs when the resin is heated in the presence of hexamethylenetetramine, which decomposes to formaldehyde and ammonia. The PU is a three-part system consisting of a P-F resin, polyisocyanate (diphenylmethane-4,4'-diisocyanate), and an amine catalyst. Once the P-F and polyisocyanate are blended, the amine gas is passed through the resin to catalyze polymerization. Furan resins are polymerized by an acid catalyst. Although the major component of furan resins is furfuryl alcohol, phenols, formaldehyde, urea, 2-furancarboxaldehyde, and 2,5-bis(hydroxymethyl)furan are often used to improve specific resin properties.^[1]

The main objective of this study was to identify major pyrolysis products of three cured foundry sand resins: Novolac, PU, and furan. The thermal decomposition products identified in this study may be similar to those found during metal casting and in waste molding sands. Because there is interest in beneficially using waste molding sands (specifically green sand, which is clay-bonded

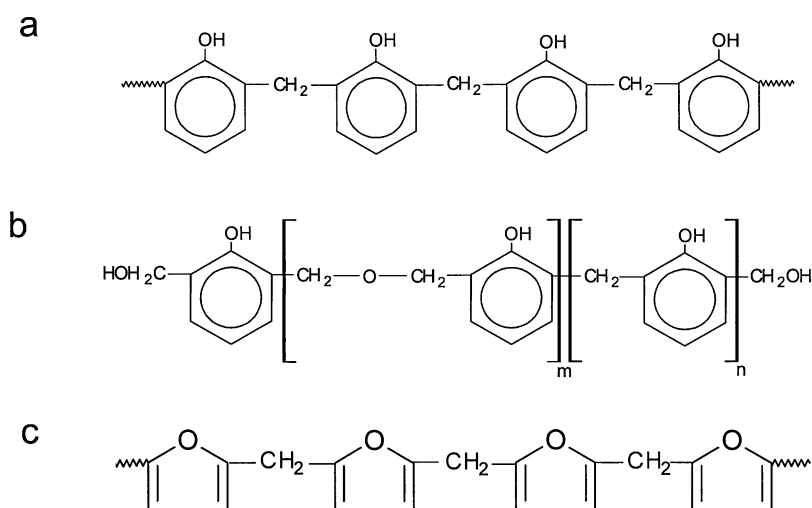


Figure 1: General structure of the (a) Novolac, (b) PU, and (c) furan resins before cross-polymerization.

silica sand) in agricultural soil blends,^[2,3] identification of potential contaminants is critical before foundry sands can be used safely in the environment. An effort was also made to confirm the presence of volatile organic pyrolysis products of environmental concern in waste molding sand (that used PU or Novolac and furan cores) using headspace-gas chromatography-mass spectrometry (Hs-GC-MS).

MATERIALS AND METHODS

Chemicals

All cores were prepared by foundries using commercial formulations. The Novolac resin (silica sand coated with 2.5% resin) was manufactured by Kore Mart LTD (Hamburg, PA, USA). The PU resin (IsocureTM 389 and 689) was manufactured by Ashland Specialty Chemical Company (Dublin, OH, USA), and the gas catalyst (triethylamine) was manufactured by HA International LLC (Westmont, IL, USA). The furan resin was manufactured by HA International LLC and the catalyst (35–38% phenol-4-sulfonic acid and <2% sulfuric acid) was manufactured by Advanced Resin Systems (Des Plaines, IL, USA). The final product contained 1.2% resin (based on sand weight) and about 15% catalyst (based on resin weight). The processes used to make the Novolac, PU, and furan cores are known as shell, cold box, and warm box, respectively.^[4] Before pyrolysis (Py) GC-MS, the hardened cores were ground to individual sand particles using a mortar and pestle.

Pyrolysis-Gas Chromatography-Mass Spectrometry

Py-GC-MS of the foundry sand resins was performed using a Chemical Data System Pyroprobe model 2000 (Oxford, PA, USA). Pyrolysis was carried out at 750°C for 30 s using a sample of 4–35 mg in quartz tubes. The pyrolysate was swept directly into a Finnigan MAT GCQ gas chromatograph coupled to a Finnigan MAT GCQ ion trap mass spectrometer (Finnigan MAT, San Jose, CA, USA). The gas chromatographic column was a DB-5ms (30 m × 0.25 mm i.d., 0.25 μm film thickness, J & W Scientific, Folsom, CA, USA) operated from 50 to 300°C at 5°C min⁻¹ holding the initial temperature for 10 min. The splitless injector temperature was 300°C. The Py-GC interface temperature was 200°C. Carrier gas (He) was held at a constant velocity of 40 cm s⁻¹. The GC-MS transfer line temperature was 300°C, and the ion trap temperature was 200°C. Mass spectra were obtained by electron impact at 70 eV from 40 to 650 *m/z* (1 scan s⁻¹). Peaks of interest eluted between 1 and 44 min (Figs. 2, 3, and 4). For tentative peak identification, mass spectra were compared with those in the NIST Mass Spectral Library (Chem SW, Version 2.0, Fairfield, CA, USA).

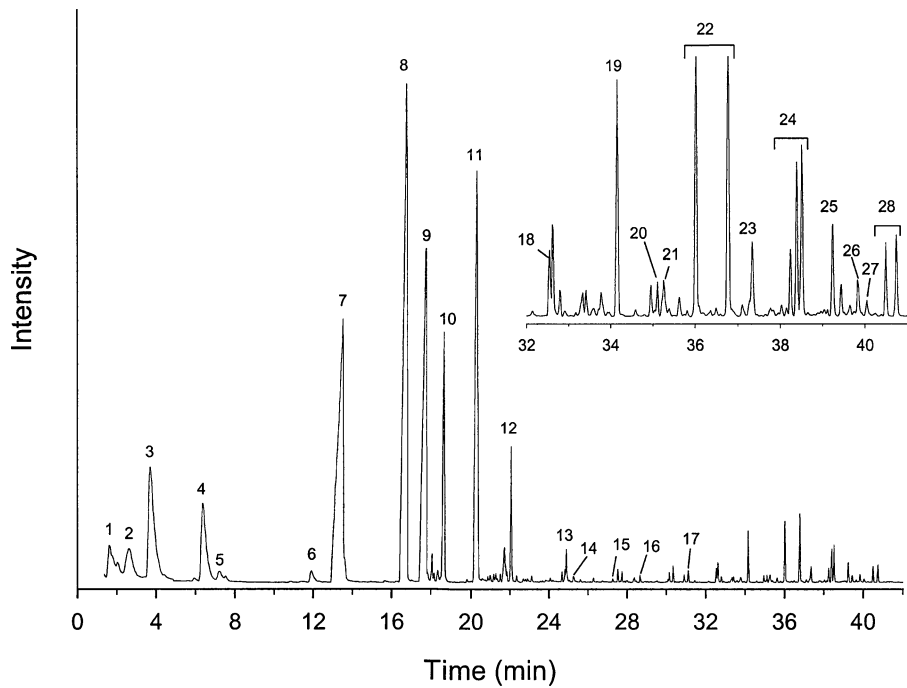


Figure 2: Gas chromatogram of pyrolysis products of cured Novolac resin.

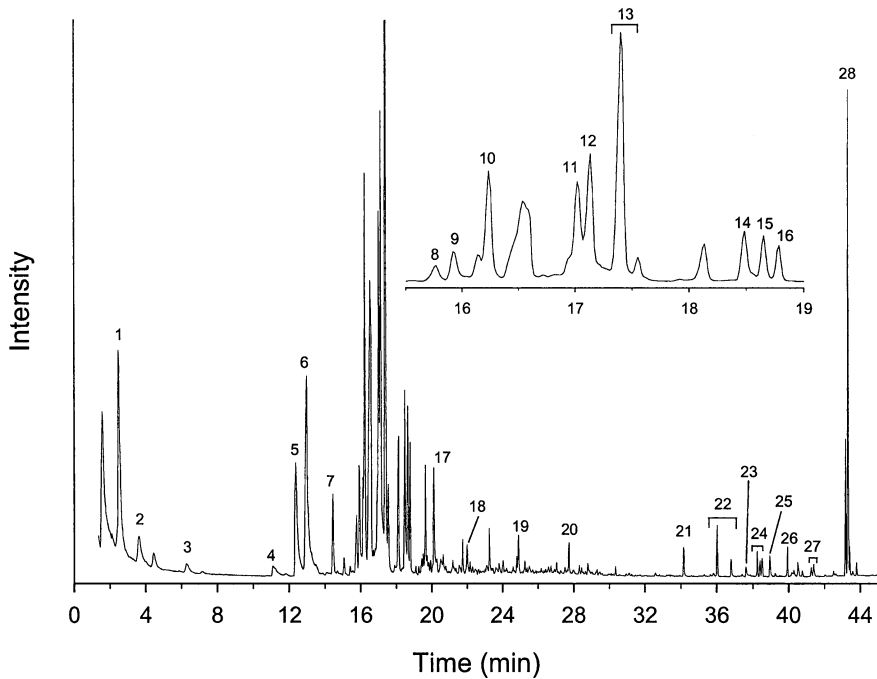


Figure 3: Gas chromatogram of pyrolysis products of cured PU resin.

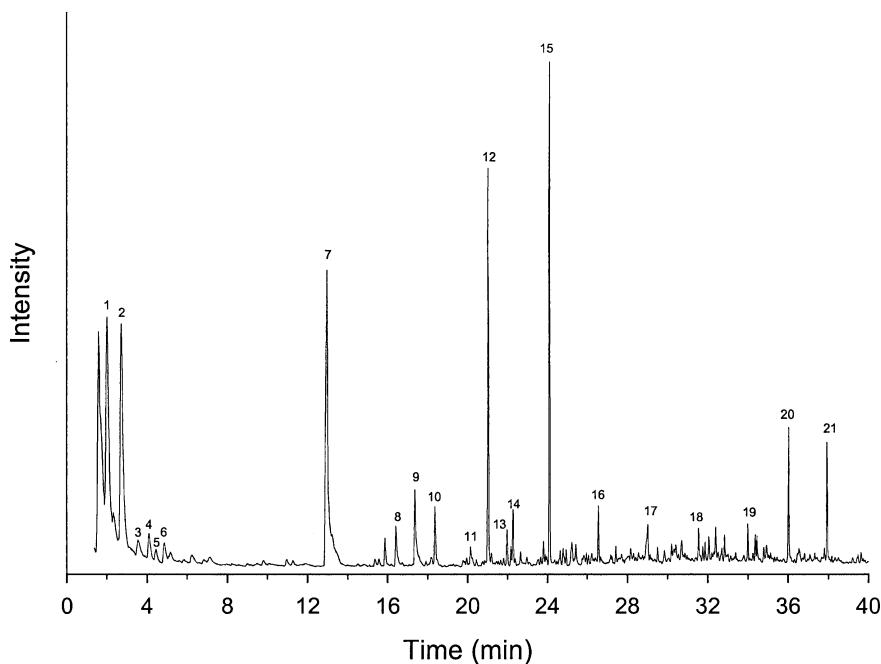


Figure 4: Gas chromatogram of pyrolysis products of cured furan resin.

Headspace-Gas Chromatography-Mass Spectrometry

To determine whether waste molding sands contained some of the volatile resin pyrolysis products, two waste molding sands (both from ferrous foundries where the resin cores were obtained) were analyzed using Hs-GC-MS. About 2 g of waste molding sand was added to a 21-mL glass headspace vial and capped with Teflon-faced septa. The vials were heated to 175°C for 3 min, and then 500 μL of the headspace was injected into a CP-3800 gas chromatograph equipped with a Saturn 2200 ion-trap mass spectrometer (Varian Inc., Palo Alto, CA, USA). The GC capillary column was a VF-5ms (30 m \times 0.25 mm \times 0.25 μm), and column injections were made using a CombiPAL autosampler (Varian Inc.). The GC conditions were as follows: injector temperature, 250°C; carrier gas, He, 1.0 mL min⁻¹; oven temperature, 40°C for 5 min, then ramping at 5°C min⁻¹ until 300°C, then 300°C for 2 min. The GC-MS transfer line temperature was 250°C, and the ion trap temperature was 150°C. Mass spectra were obtained by electron impact at 70 eV from 40 to 300 m/z (1.7 scans s⁻¹). Volatile organics were identified using the NIST Mass Spectral Library.

RESULTS AND DISCUSSION

The pyrolysis of foundry sand resins at 750°C was conducted to identify thermal decomposition products that may be produced during the metal casting process.

Because of the very high temperature of the molten metal, pyrolysis of the core resin is nearly complete at the metal–core interface. Further from the metal interface into the core, partial decomposition can be expected.^[5] In this study, thermal decomposition products from the P-F (Novolac and PU) and furfuryl alcohol (furan) resins were tentatively identified by their mass spectra. The gas chromatograms for each of the resins are shown in Figures 2, 3, and 4. Tables 1, 2, and 3 list the respective compounds identified in the pyrolysates and their molecular weights.

During thermal decomposition of P-F resins, the bonds between aromatic rings and methylene bridges are broken.^[6] Lytle et al.^[7] determined that 59% and 71% of a Novolac resin (a sand initially containing 3.0% resin) are lost when pyrolyzed at 750 and 980°C, respectively. In this study, pyrolysis of the Novolac resin generated over 50 different products (Fig. 2). Our results reveal that a large number of the decomposition products were phenolic compounds, including phenol and various methyl substituted phenols (nos. 7–13). Phenolic compounds have been identified in other reports when Novolac resin was pyrolyzed under similar conditions.^[6–8] The most intense peak was 2-methylphenol (*o*-cresol), followed by 3,5-dimethylphenol, 3-methylphenol

Table 1: Peak identification of pyrolysis products of Novolac resin.

No.	Compound name	MW
1	Ethylamine	45
2	Benzene	78
3	Toluene	92
4	<i>o</i> -Xylene	106
5	<i>p</i> -Xylene	106
6	1,3,5-Trimethylbenzene	120
7	Phenol	94
8	2-Methylphenol	108
9	3-Methylphenol	108
10	2,3-Dimethylphenol	122
11	3,5-Dimethylphenol	122
12	2,4,6-Trimethylphenol	136
13	4-Cyano-3,5-dimethylphenol	147
14	2-Methylnaphthalene	142
15	2-Ethenylnaphthalene	154
16	2-Methyl-1,1'-biphenyl	168
17	2,2'-Dimethylbiphenyl	182
18	Fluorene	166
19	9H-Xanthene	181
20	2-Methyldodecane	184
21	3-Methyl-9H-fluorene	180
22	(2-Methylphenyl)-phenylmethanone	196
23	9-Methylene-9H-fluorene	178
24	2,4-Dimethylbenzophenone	210
25	2,5-Dimethylbenzophenone	210
26	2-Methylphenanthrene	192
27	1-Methylantracene	192
28	2,4,6-Trimethylbenzophenone	224

Table 2: Peak identification of pyrolysis products of PU resin.

No	Compound name	MW
1	Triethylamine	101
2	Toluene	92
3	<i>o</i> -Xylene	106
4	2-Hydroxybenzonitrile	119
5	Aniline	93
6	Phenol	94
7	1,2,3-Trimethylbenzene	120
8	1,4-Diethylbenzene	134
9	1-Methyl-3-propylbenzene	134
10	2-ethyl-1,4-dimethylbenzene	134
11	1-Methyl-3-(1-methylethyl)-benzene	134
12	1-Methyl-4-(1-methylethyl)-benzene	134
13	1-Methyl-2-(1-methylethyl)-benzene	134
14	2,3-Dimethylphenol	122
15	1,2,3,5-Tetramethylbenzene	134
16	1-Ethyl-3,5-dimethylbenzene	134
17	3,5-Dimethylphenol	122
18	2,4,6-Trimethylphenol	136
19	2,3,5,8-Tetramethyldecane	198
20	1-Iodo-2-methyldecane	296
21	9H-Xanthene	182
22	(2-Methylphenyl)phenylmethanone	196
23	Acridine	179
24	2,4- and 2,5-Dimethylbenzophenone	210
25	9-Methylacridine	193
26	2,4-Dimethylbenzo(h)quinoline	207
27	10,13-Dimethyl-, methylester tetradecanoic acid	270
28	Octadecenoic acid (z)-, methylester	296

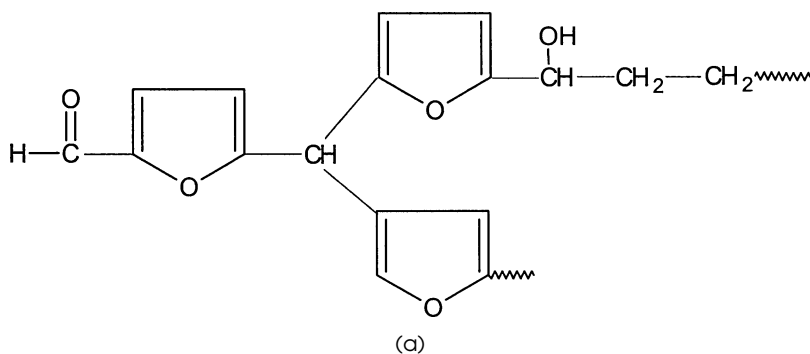
Table 3: Peak identification of pyrolysis products of furan resin.

No.	Compound name	MW
1	3,5-Pentadienal	82
2	2,5-Dimethylfuran	96
3	Toluene	92
4	1-(2-Furanyl)-ethanone	110
5	2,3,5-Trimethylfuran	110
6	3-Methylphenol	108
7	Phenol	94
8	2-Methylphenol	108
9	2,2'-Methylenebisfuran	148
10	2-Methylbenzofuran	132
11	3,5-Dimethylphenol	122
12	2-(2-Furanylmethyl)-5-methylfuran	162
13	5,6-Dimethyl-1-H-benzimidazole	146
14	4,7-Dimethylbenzofuran	146
15	2,2'-Methylenebis(5-methylfuran)	176
16	5-(5-Methyl-2-furanyl)methyl-2-furancarboxaldehyde	190
17	3,3-Dimethyl-2(3H)-benzofuranone	162
18	2-Methoxy-3-benzofurancarboxaldehyde	176
19	2,5-Bis(2-furanylmethyl)-furan	228
20	2,2'-(2-Furylmethylene)bis(5-methylfuran)	242
21	2-Piperidino-8-nitro-1,4-naphthoquinone	286

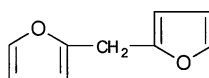
(*m*-cresol), phenol, 2,3-dimethylphenol, and then 2,4,6-trimethylphenol. Volatile aromatics identified in the pyrolysates were benzene, toluene, *o*- and *p*-xylene, and 1,3,5-trimethylbenzene (nos. 2–6). Polynuclear aromatic products containing two or more condensed rings were 2-methylnaphthalene, 2-ethenylnaphthalene, fluorene, 3-methyl-9H-fluorene, 9-methylene-9H-fluorene, 2-methylphenanthrene, and 9H-xanthene. Sobera and Hetper^[8] postulated that xanthenes were created through a cyclization reaction with participating hydroxyl or methyl groups in an *ortho* position relative to the methylene bridges. The presence of xanthenes and related derivatives is characteristic for cured Novolac and Resole resins. In contrast to the Novolac resin, Resole resin is formed when excess formaldehyde is combined with phenol under basic conditions. Because cured Novolac and Resole resin are structurally alike, thermal decomposition products are similar between these resins.^[8]

When PU resin is cured using amine gas, it is known as the PU cold box (PUCB) method and is termed the IsocureTM process in the United States.^[9] Although the Novolac and PUCB resin are both P-F based resins, the thermal decomposition products differed considerably. Instead of phenolics, various methyl, ethyl, and propyl substituted benzenes were the major pyrolysis products identified from the PU resin (Fig. 3, nos. 7–13, 15, and 16). The most abundant peak (no. 13) was identified as 1-methyl-2-(1-methylethyl)-benzene. Other abundant thermal decomposition products were 2-ethyl-1,4-dimethylbenzene, 1-methyl-3-(1-methylethyl)-benzene, and 1-methyl-4-(1-methylethyl)-benzene (nos. 10–12). In addition to phenol, the only phenolic compounds identified were 2,3-dimethylphenol, 3,5-dimethylphenol, and 2,4,6-trimethylphenol, which were also identified as pyrolysis products of Novolac resin. Polynuclear aromatic compounds identified were acridine, 9-methylacridine, 2,4-dimethylbenzo(h)quinoline, and 9H-xanthene. The volatile organics consisted of triethylamine, toluene, *o*-xylene, and aniline. It is suspected that the presence of triethylamine is not a pyrolysis product but a residual gas catalyst used to cure the resin, whereas aniline is used to produce the polyisocyanate, diphenylmethane-4,4'-diisocyanate.^[9]

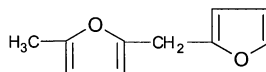
The pyrolysis of furan resin resulted in the generation of 12 furan based compounds, with molecular weights ranging from 96 (dimethylfuran; no. 2) to 242 (2,2'-(2-furylmethylene)bis(5-methylfuran); no. 20) (Fig. 4). Of these products, the most abundant compounds were 2-(2-furanylmethyl)-5-methylfuran (no. 12) and 2,2'-methylenebis(5-methylfuran) (no. 15). Figure 5a shows the proposed structure of cured furan resin^[10]; Figure 5b shows the structure of several thermal decomposition products that contain two and three furan rings. The generation of products such as 2,5-dimethylfuran and 2,3,5-trimethylfuran (nos. 2 and 5) suggests that thermal decomposition of the furan resin consists of breaking the methylene bridges between the furan rings. The cleaved methylene bridges of the furan resin form radical groups that join with hydrogen to produce methylfurans. Phenol was also highly abundant, which may have



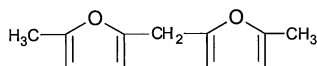
2,2'-Methylenebisfuran



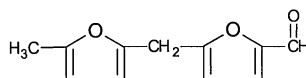
2-(2-Furanylmethyl)-5-methylfuran



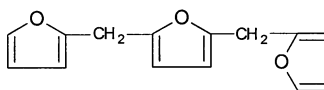
2,2'-Methylenebis(5-methylfuran)



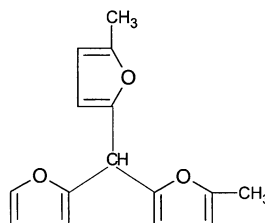
5-(5-Methyl-2-furanyl)methyl-2-furancarboxaldehyde



2,5-Bis(2-furanylmethyl)-furan



2,2'-(2-Furylmethylene)bis(5-methylfuran)



(b)

Figure 5: (a) Representative chemical structure of cured furan resin. (b) The chemical structure of select pyrolysis products of cured furan resin.

been an additive in the resin; however, this is often proprietary information.^[1] Other phenolics identified include 2-methylphenol (*o*-cresol), 3-methylphenol (*m*-cresol), and 3,5-dimethylphenol.

CONCLUSIONS

Py-GC-MS is a useful technique to characterize thermal decomposition products from foundry resin binders and could also serve to examine waste molding sands for intact polymer residues by identifying signature pyrolysis products. Because there is interest in using foundry sands in agricultural/horticultural products such as manufactured soils, identifying potential contaminants before these materials are used in the environment is essential for protection of ground and surface waters. Of the pyrolysis products identified in this study, benzene, toluene, and xylenes raise the most concern because they are regulated under the National Primary Drinking Water Standards by the U.S. Environmental Protection Agency (EPA).^[11] Additionally, polynuclear aromatic hydrocarbons (2-methylnaphthalene, 2-ethylnaphthalene, fluorene, 3-methyl-9H-fluorene, 9-methylene-9H-fluorene, and 2-methylphenanthrene), 2-methylphenol (*o*-cresol), 3-methylphenol (*m*-cresol), and phenol were identified and are included on the EPA's priority list. Of the EPA regulated compounds, all were thermal decomposition products of the Novolac resin, whereas only four or fewer were products of the PU and furan resins. In waste molding sands that used cores with these resin binders, the presence of the following volatile organics was tentatively confirmed by Hs-GC-MS: benzene, toluene, phenol, and *o*- and *p*-xylene (data not shown). Further research will be directed toward quantifying these and other regulated compounds (volatile, semivolatile, and nonvolatile organics) in an assortment of waste molding sands.

ACKNOWLEDGMENTS

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